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# EFFECT OF SURFACE TOPOGRAPHY ON STRUCTURAL GROWTH OF THICK SPUTTERED FILMS

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# EFFECT OF SURFACE TOPOGRAPHY ON STRUCTURAL GROWTH OF THICK SPUTTERED FILMS

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## SUMMARY

Thick sputtered S-Monel, silver, and 304 stainless steel coatings were deposited on mica, glass, and metal substrates with various surface finishes to investigate the structural growth of the coating by scanning electron microscopy. Compositional changes within the coating were analyzed by X-ray dispersion microscopy. Defects in the surface finish (i.e., scratches, inclusions, etc.) act as preferential nucleation sites and form isolated and complex nodules and various surface overgrowths in the coating. These nodules do not disappear after full annealing. Further, they have undesirable effects on mechanical properties; cracks are initiated at the nodules when the coating is stressed by mechanical forces. These effects are illustrated by micrographs. Nodular growth within a coating can be minimized or eliminated by reducing the surface roughness.

## INTRODUCTION

With the achievement of high vapor deposition rates and the improvement in sputtering equipment to yield higher sputtering rates, an increased interest has developed in thick vapor-deposited and sputtered coatings. Relatively thick (2.5- to 50- $\mu\text{m}$ ) coatings vapor-deposited at high speed are beginning to be applied commercially in free-standing shapes such as foil, sheet, and tubing (ref. 1). A very limited number of studies have been conducted relative to the structural growth of these thick coatings. Most structural growth studies have been concerned with thin films.

Generally, thick coatings formed by vapor deposition have a columnar growth with a preferred orientation of the elongated grains toward the source of vapor.

This columnar growth usually becomes pronounced when the coating thickness becomes greater than about 1 micrometer.

It has also been reported that thick metallic coatings deposited by electroplating reveal very unusual structural formations such as nodular growth and various complex surface overgrowths (ref. 2). These structural incongruities normally present an unacceptable condition when the coatings are exposed to mechanical forces. It is well established (ref. 3) that not only the physical, electrical, and magnetic properties but also the mechanical properties such as strength, toughness, and ductility are strongly influenced by the film microstructure. Therefore, a controlled structural growth should be maintained during the deposition process.

With the increased interest in commercial sputtering, applications of thick sputtered coatings are being considered for practical uses. Because of the relatively low sputtering rates, normally in the range  $50 \times 10^{-10}$  to  $5000 \times 10^{-10}$  meter per minute ( $50$  to  $5000 \text{ \AA}/\text{min}$ ), most of the film research has concentrated on thicknesses in the low micrometer range ( $<1 \text{ }\mu\text{m}$ ). Presently there are no systematic studies reported in the literature on the structural growth and the factors influencing growth with increasing thickness. Several investigations have discussed the structural growth of thick sputtered coatings by varying the various sputtering parameters and the substrate temperature (refs. 4 and 5). Many of the growth features are similar to those for vapor-deposited coatings. However, it should be realized that the sputtered coatings grow in a much more complex environment than the vapor-deposited coatings. Factors which generally affect film formation during sputtering are (1) kinetic energy of the sputtered species, (2) plasma conditions, (3) substrate temperature, (4) surface topography, and (5) specimen potential. Since the surface is the starting point for film growth, surface condition (roughness, inhomogeneities, impurities, etc.) has a direct effect on film structure. Inhomogeneities, impurities, steps, etc. are favorable sites for nucleation. However, it is impossible to prepare a metallic surface which is atomically smooth over an appreciable area. Dislocation lines and surface point defects limit the best surface achievable.

The objective of this study was to examine the microstructure and the chemical composition of thick sputtered coatings by scanning electron microscopy (SEM) and X-ray dispersion microscopy. The influence of annealing and mechanical forces on these coatings was also examined. The thick coatings ( $12.5$  to  $37.5 \text{ }\mu\text{m}$ ) were primarily S-Monel, silver, and 304 stainless steel. The substrates were

mica, glass, and polished, sanded, and sandblasted bronze surfaces.

## APPARATUS AND PROCEDURE

The sputtering apparatus used in this study was a radiofrequency-diode system with a superimposed direct-current bias, as shown in figure 1. This apparatus is described in references 6 and 7. The sputtering target was a 12.7-centimeter-diameter S-Monel disk (composition in percent: nickel, 63; copper, 30; iron, 2; manganese, 0.5; silicon, 4; carbon, 0.1). The sputtering conditions were kept constant with a radiofrequency power density of 3.5 watts per square centimeter at 7 megahertz and an argon pressure of 20 millitorr. The specimen during the deposition was maintained at ground potential relative to the target. The substrates used were glass, freshly cleaved mica, bronze, and copper. The metal specimens were (2 by 2 by 0.025 cm) sheets with various surface finishes. These consisted of (1) lapping on a polishing wheel with a resultant surface finish of  $5 \times 10^{-2}$  micrometer (2  $\mu$ in.), (2) grinding on a 600 grit emery paper with a resultant surface finish of  $22.5 \times 10^{-2}$  micrometer (9  $\mu$ in.), and (3) sandblasting. Prior to sputter deposition, all metal surfaces were direct-current-sputter-cleaned for about 10 minutes. The distance between the target and the specimen was 2.5 centimeters. A Chromel-Alumel thermocouple was imbedded in the specimen, and the temperature was maintained at 145<sup>o</sup> C. Coating thicknesses ranged from 12.5 to 37.5 micrometers (0.5 to 1.5 mils). The surface topography and the cross section of the coatings were examined by SEM, and the chemical composition was determined by X-ray dispersion microscopy.

## RESULTS AND DISCUSSION

### Characterization of Sputtered S-Monel Coatings by Scanning Electron Microscopy

Examination of sputtered S-Monel coatings on metal surfaces by SEM showed the formation of nodules in the coating matrix. Typical scanning electron micrographs in figure 2 show fracture cross sections of the coating with the nodules.

It was observed that the frequency of distribution and size of the nodules changed from sample to sample, while the sputtering conditions remained constant. As shown in figure 2 all the nodules, regardless of their size, had a cone shape. A typical nodule is constructed as shown in figure 3. The surface of the nodule is a circular arc, and it projects above the surface by a distance  $h$ . The diameter of the nodule  $d$  increases as the film thickness  $t$  increases. The boundary of the nodule is parabolic in shape, which indicates an ever-increasing size with continuing deposition. These nodules have a tendency to grow in size with an increase in film thickness. At surface defects the nodules grow faster than on the rest of the deposit. The primary driving force which is responsible for the nodular growth is believed to be the surface defects which act as preferred nucleation sites exhibiting an increased growth rate.

Surface roughness effects on coating structure. - In order to establish the nature of deposit growth on very smooth surfaces, freshly cleaved mica sheets and microscope glass slides were used as substrates. The film structures formed on mica and glass slides were examined by SEM, and a typical cross section of these deposits is shown in figure 4. These deposits have a uniform columnar pattern without nodular growth.

Metallic surfaces of brass and copper with different surface roughnesses were used to investigate topographical effects on structural growth. Figure 5 shows a surface of S-Monel coating sputtered on a brass specimen where one section was highly polished (to  $5 \times 10^{-2} \mu\text{m}$ ;  $2 \mu\text{in.}$ ) and the other section was sandblasted. The figure reveals a distinct difference in the coating topography due to the surface roughness effects which are transmitted through the coating. The coating on the sandblasted section of the specimen shows considerable roughness with a high concentration of nodules. The coating on the polished section shows a featureless surface structure. Figure 6 shows surface views of a sputtered coating on a brass substrate sanded with a 600 grit abrasive paper to a surface finish of  $22.5 \times 10^{-2}$  micrometer ( $9 \mu\text{in.}$ ) at two magnifications. The nodules have a tendency to form preferentially in high concentrations along the edge boundaries of the scratches, which are favorable sites for nucleation. A high degree of nodule overlapping or partial fusion is also seen at these locations.

Annealing effects on coating structure. - As surface roughness increases, residual stresses also increase. These stresses may act as nucleation inducers

to increase nucleation rates and the subsequent growth of nodules. To determine the influence of surface residual stress effects produced during sanding on nodular growth, the sanded specimens were completely annealed (at  $810^{\circ}$  to  $870^{\circ}$  C) before the coating was sputter-deposited. A surface micrograph of one of the specimens with this sputtered coating is shown in figure 7. The film retains the nodular growth. This result implies that the surface stresses are not the primary contributing factors for the nodular growth.

Another approach was taken to determine the effect of postdeposition annealing on the behavior of these nodules. It was found that after full annealing in vacuum at temperatures of  $870^{\circ}$  C the nodules did not change or disappear, as shown in figure 8. The only observable change is the surface faceting caused by the high temperature.

From figures 7 and 8 it appears that nodular growth is associated with surface defects rather than surface stresses. Nucleation studies of vapor-deposited films reveal (ref. 8) that nucleation is indeed favored at steps or ledges on the surface and suggest that the nucleation rate is also influenced at these sites. For instance, the scratch edges inclined at various angles to the flat portion of the crystal exhibit different nucleation rates and subsequent grain growth. It is interesting to note that the growth from the edges of the depressions overtakes growth from the bottoms of the depressions and prevents continuation of growth from the latter regions (ref. 9).

Chemical analysis of S-Monel coating. - X-ray dispersion micromaps were taken of the coating matrix and nodule. No composition changes were detected in S-Monel. These results indicated that the sputtered S-Monel coating had uniform composition distribution.

Sputtered coatings of silver and 304 stainless steel. - In order to examine the coating material effects on metallic surfaces, an elemental metal, silver, and a complex alloy, 304 stainless steel, were sputter-deposited. As a result similar coating structural growth with nodule formation was also observed with silver and 304 stainless steel sputtered on metal surfaces. A typical surface view of sputtered silver nodules composed of polyhedron crystals on copper is shown in figure 9. Sputtered 304 stainless steel on brass forms nodules and surface overgrowths around scratch marks, as shown in figure 10.

## Complex Surface Outgrowths

In addition to the individual nodular growth, more complicated structural growths are formed on coatings, as shown in figures 11 and 12. Substrate defects, inhomogeneities, or impurities are believed to be the cause for extreme localized growth. The very common surface growth shown in figure 11 is a result of the interference of adjacent nodules during the growth process. Certain nodules have a preferential growth and thus effectively overwhelm their neighbors and form a cauliflower structure. The basic mechanism for this type of growth formation is not clear, but it is possible that the primary nodules when formed are subnucleating and thus produce this cauliflower structure. Figure 12 shows a wormlike surface growth at two magnifications.

### Effect of Nodular Structure on Fracture Characteristics

It was observed that, when a nodule reaches a critical diameter on the surface and when the film is exposed to mechanical forces such as bending, the coating will have a tendency to break around the nodule edges (fig. 13), but not through the nodule. The nodule can simply be ejected from its place and leave an empty cavity, as shown in figure 14. The nodules exert localized stresses in the coating and thus act as sources for cracks. The size of the nodules has an apparent effect on the mechanical properties. As the coating thickness increases, the size of the nodule also increases. For thin films the nodules are very small and their effects are less detrimental. The bending tests show that strict control should be exercised in obtaining the desired structure by carefully preparing the surface finish before sputter deposition. The nodular effects on mechanical properties have been discussed for thermally deposited pyrolytic graphite films (ref. 10). It has been shown that these nodules exert localized residual tensile stresses in the coating.



## SUMMARY OF RESULTS

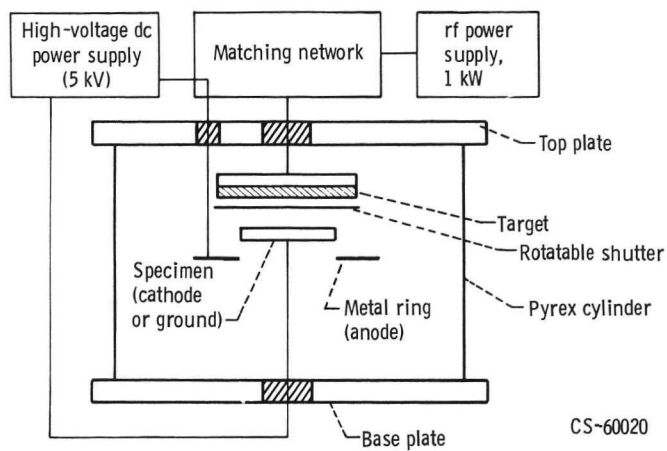
The structural growth of thick S-Monel, silver, and 304 stainless steel coatings sputtered at constant sputtering conditions on surfaces with various finishes was evaluated by scanning electron microscopy and X-ray dispersion microscopy. Annealing and bending experiments were also performed on these coatings. The following results were obtained from this investigation:

1. On smooth mica, glass, and highly polished ( $5 \times 10^{-2} \mu\text{m}$ ;  $2 \mu\text{in.}$ ) metallic surfaces, the sputtered coating had a columnar structure.
2. Surface defects on metals (scratches, inclusions, impurities, etc.) acted as preferential nucleation sites and as a result isolated nodules, complex nodular type structures, and various surface overgrowths were formed. The size of the nodules increased as the thickness of the coating increased.
3. The nodules within the deposit did not disappear after full annealing.
4. Nodules and complex surface overgrowths in the coating had undesirable effects on mechanical properties, since they acted as stress raisers and initiated cracks.
5. The coating material did not affect nodular formation. Nodular growth was observed with elemental metals and with complex alloys.
6. No compositional changes were observed inside or outside the nodules in sputtered S-Monel coatings.
7. Nodular growth can be minimized or eliminated by reducing the surface roughness.

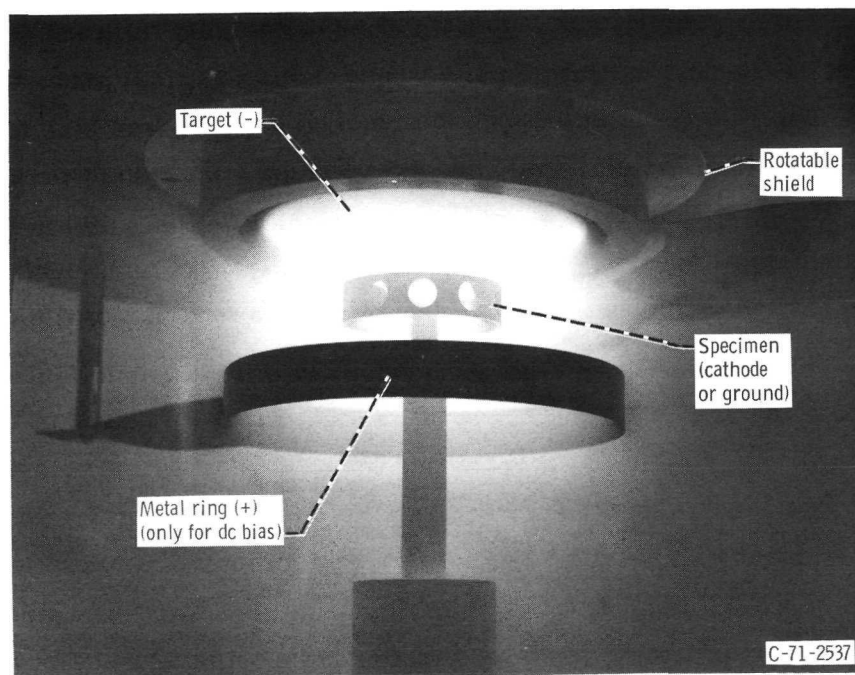
Lewis Research Center,  
National Aeronautics and Space Administration,  
Cleveland, Ohio, November 20, 1973,  
502-21.

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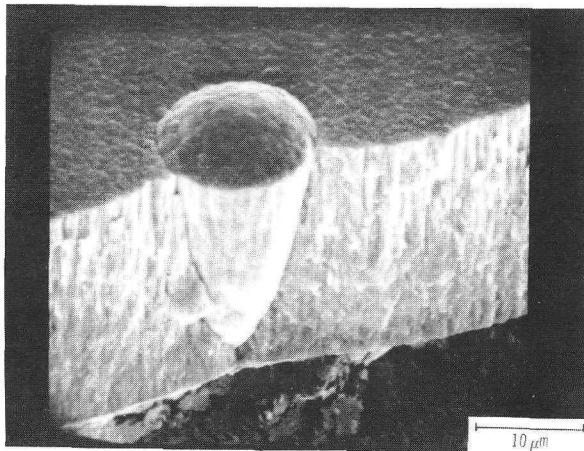


(a) Schematic diagram.

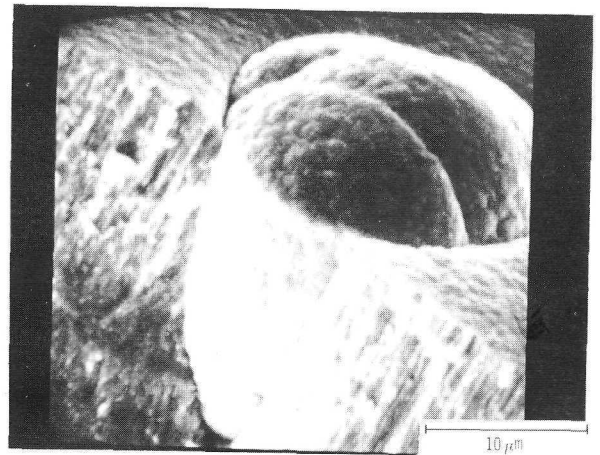


(b) View of apparatus during sputter coating.

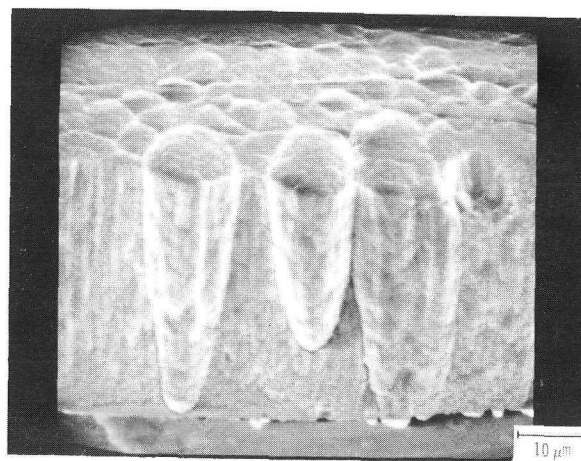
Figure 1. - Radiofrequency diode sputtering apparatus with direct-current bias.



(a) Isolated nodule.



(b) Fused nodules.



(c) Cluster of nodules.

Figure 2. - Fracture cross sections of nodular growth in S-Monel brass.

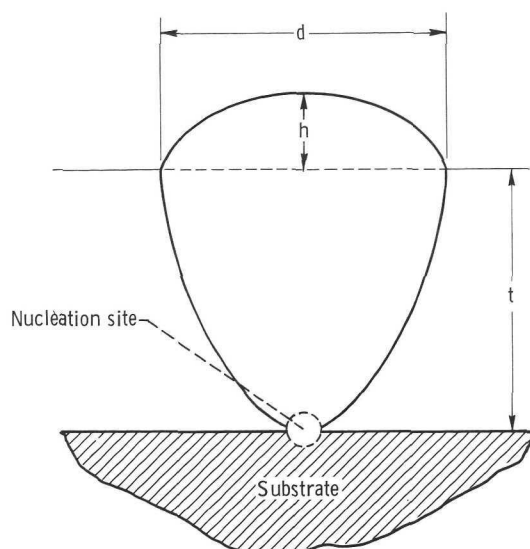


Figure 3. - Geometric construction of typical isolated nodule. Film thickness,  $t$ ; diameter of nodule,  $d$ ; height of nodule above surface,  $h$ .

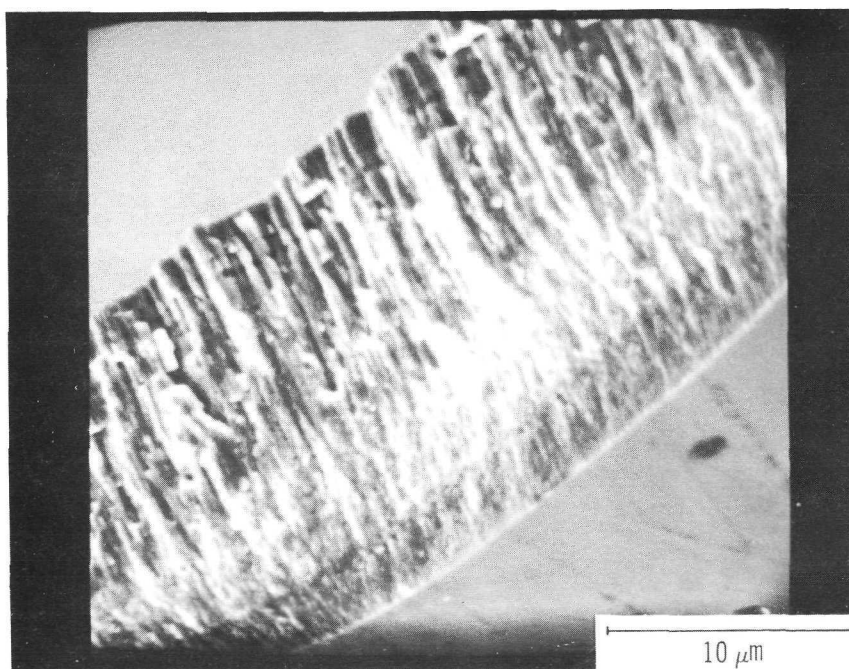


Figure 4. - Typical cross section of sputtered S-Monel on mica.

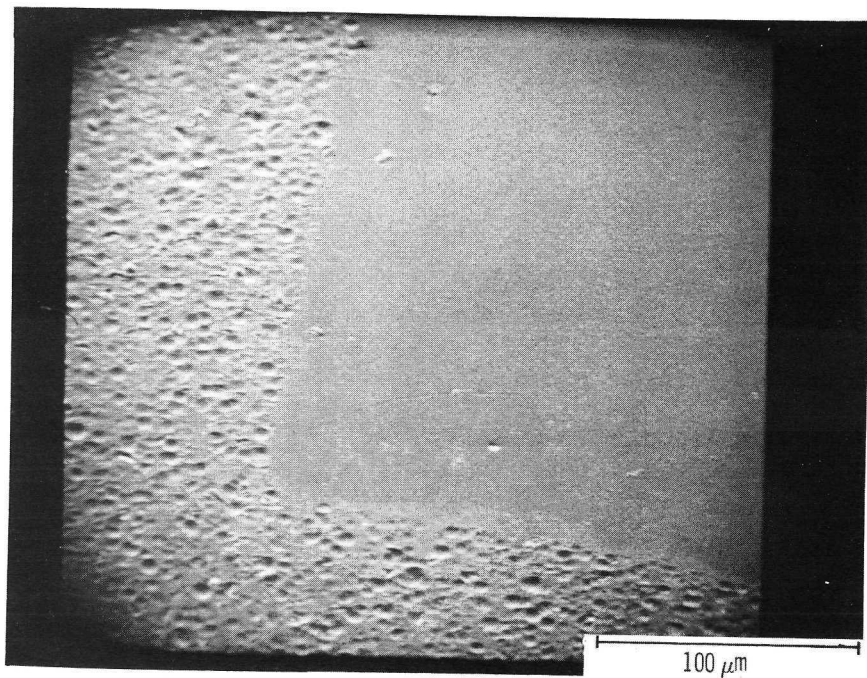


Figure 5. - Surface of sputtered S-Monel coating on smooth and sandblasted sections of brass surface.

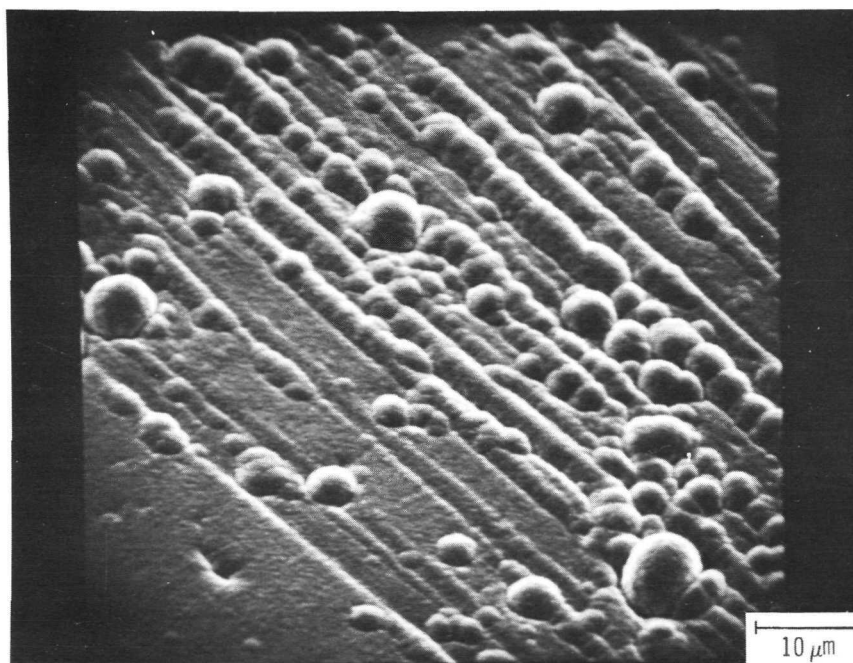
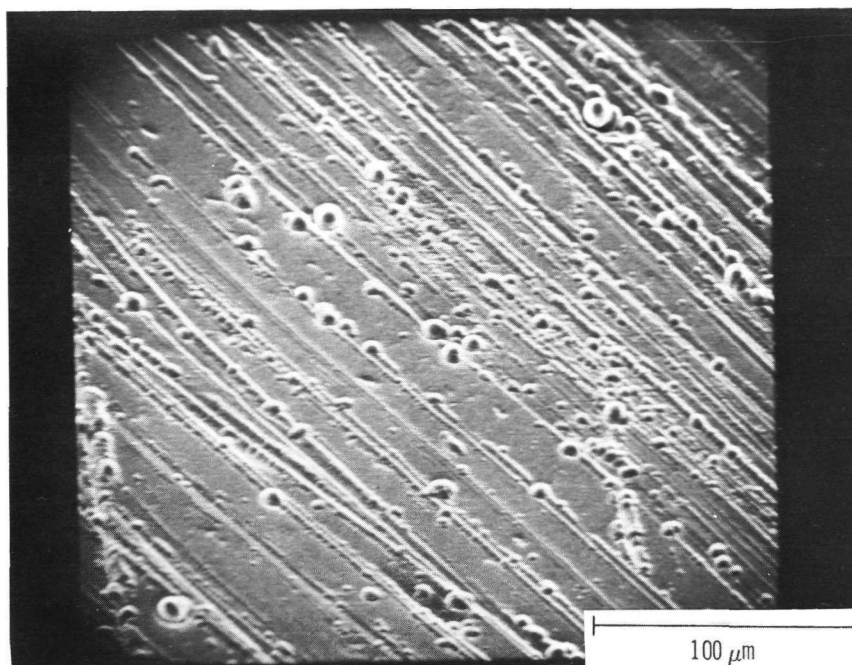


Figure 6. - Surface of sputtered S-Monel on brass surface sanded to  $22.5 \times 10^{-2}$ -micrometer finish.



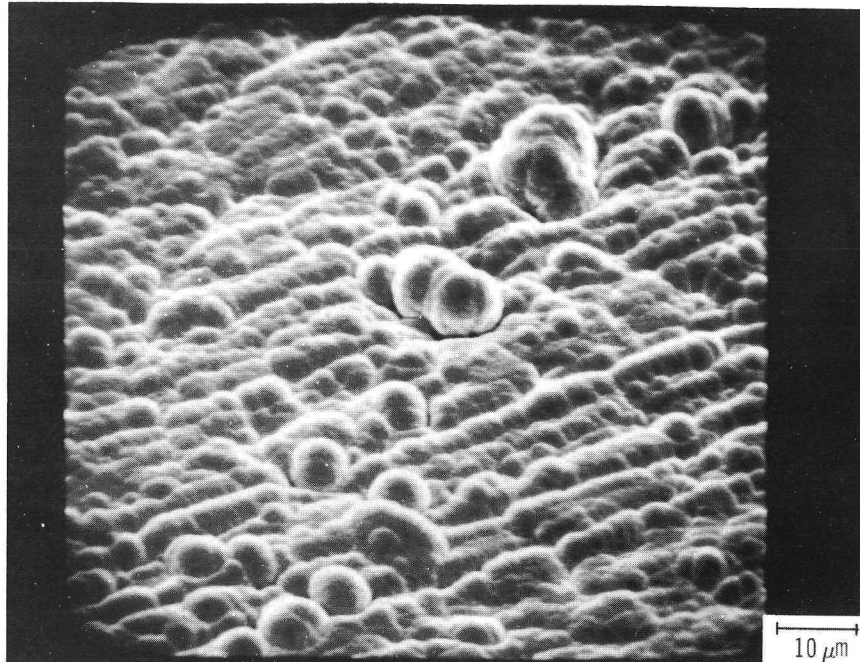


Figure 7. - Surface of sputtered S-Monel on brass surface sanded to  $22.5 \times 10^{-2}$ -micrometer finish and subsequently annealed at  $870^{\circ}\text{C}$  before deposition.

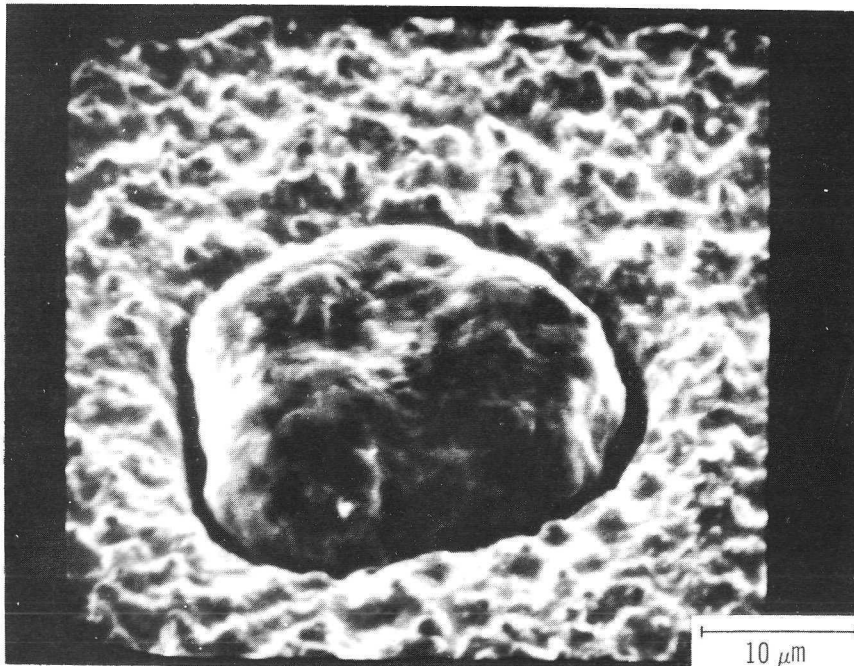


Figure 8. - Surface of sputtered S-Monel on brass after full annealing at  $870^{\circ}\text{C}$  in vacuum.



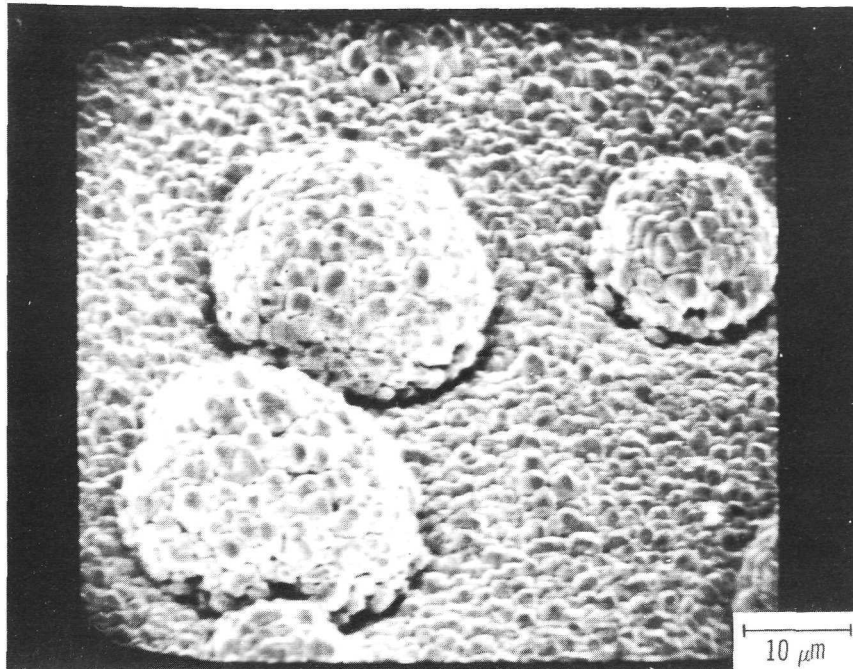


Figure 9. - Surface of sputtered silver on copper.

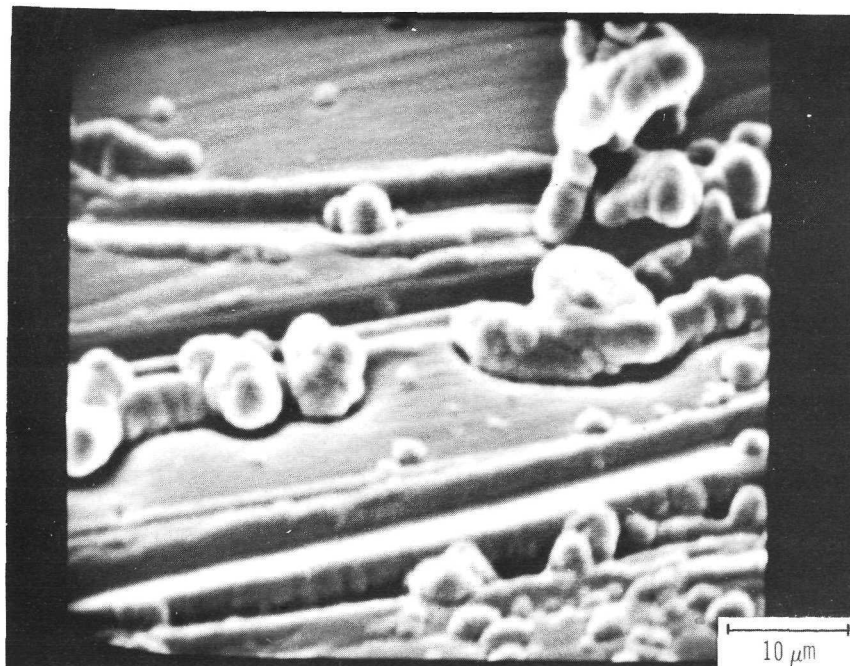


Figure 10. - Surface of sputtered 304 stainless steel on brass.

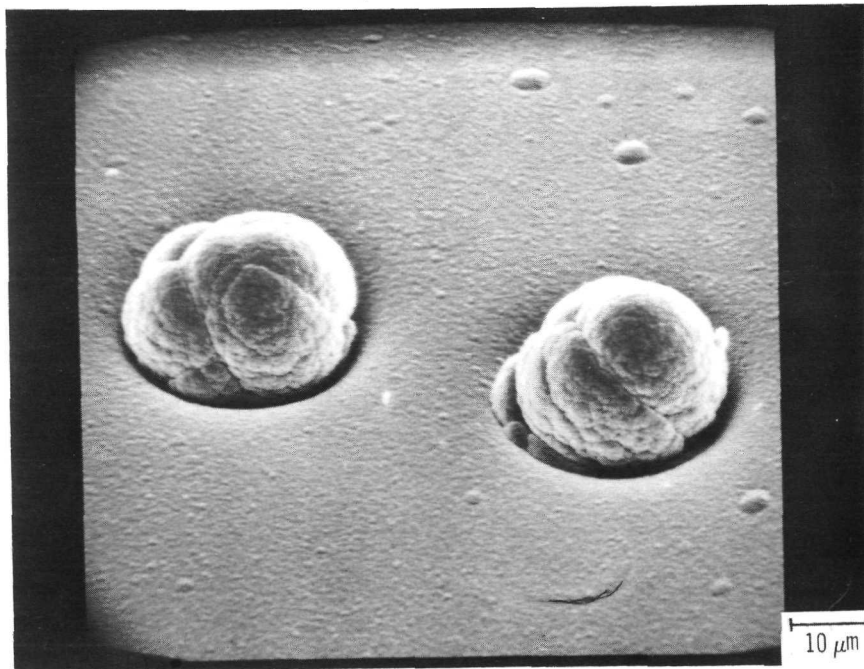
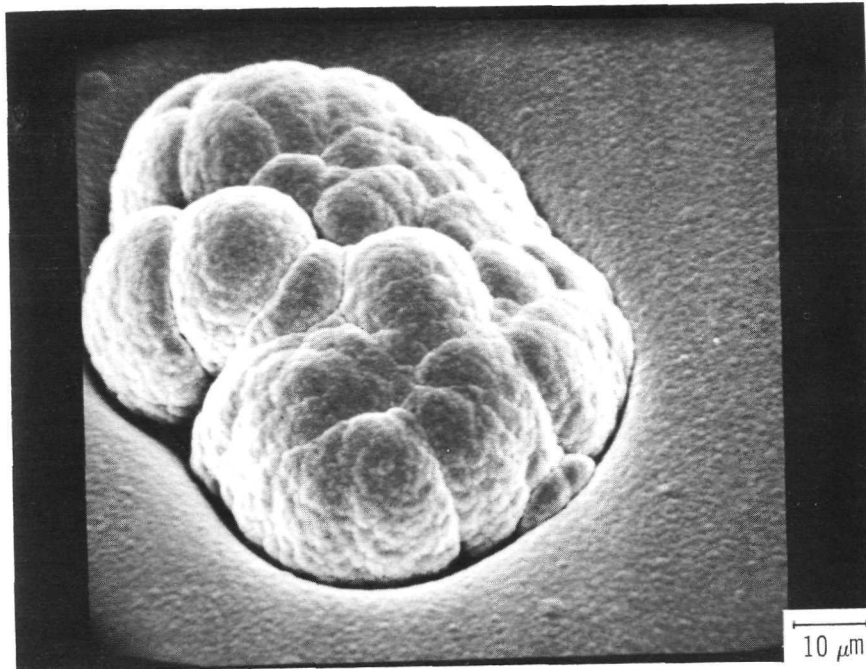


Figure 11. - Surface outgrowths with typical cauliflower structures in sputtered S-Monel on brass.

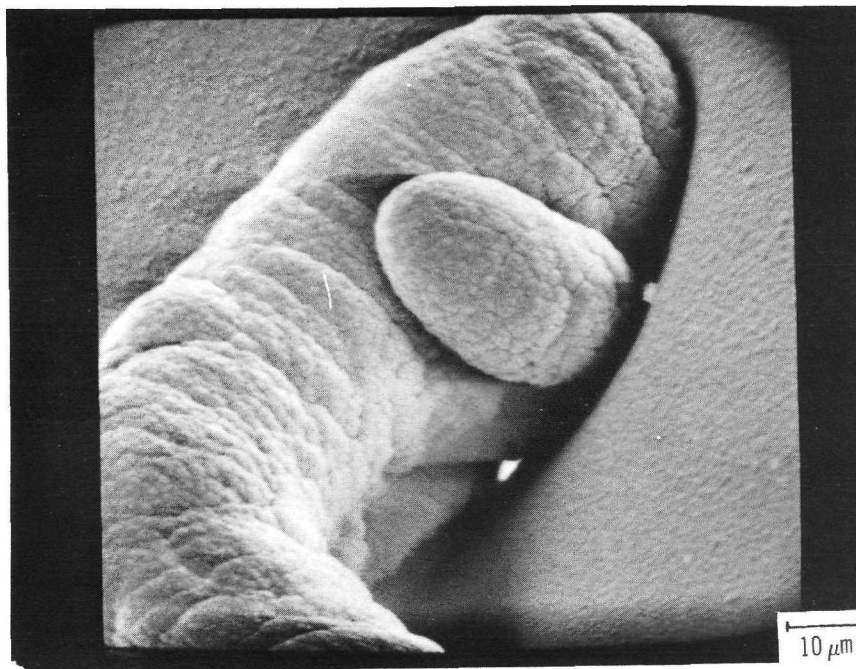
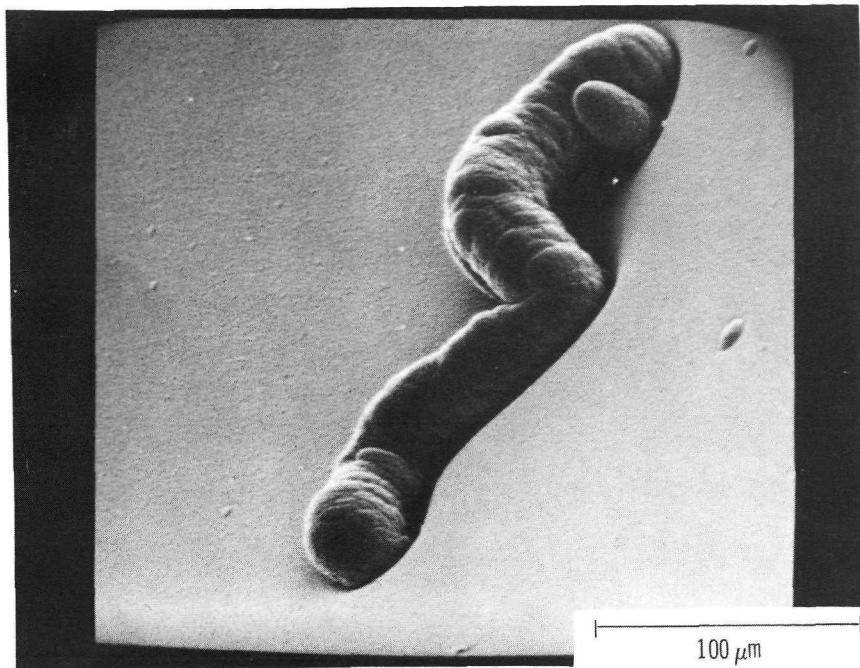


Figure 12. - Surface outgrowth of wormlike structure in sputtered S-Monel on brass.

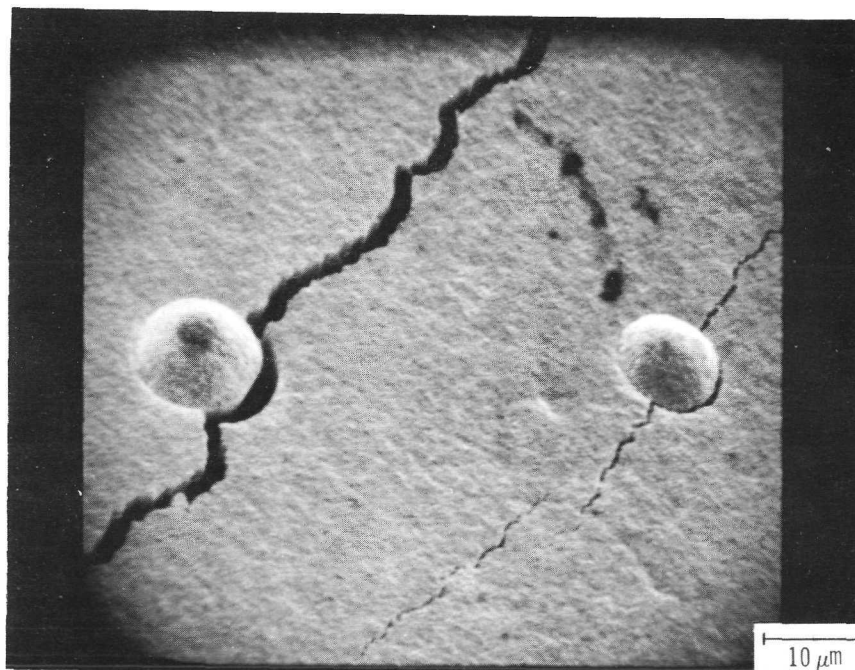
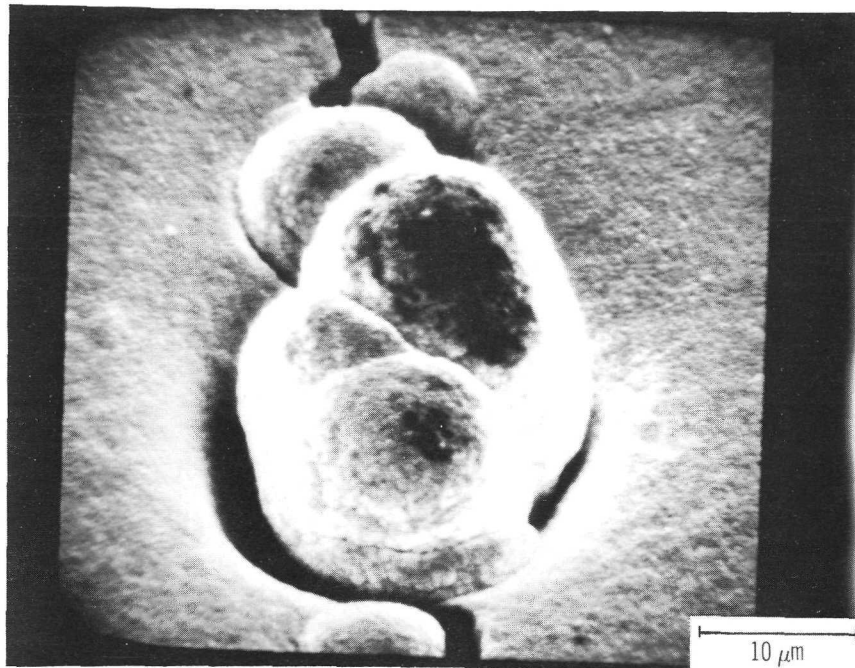
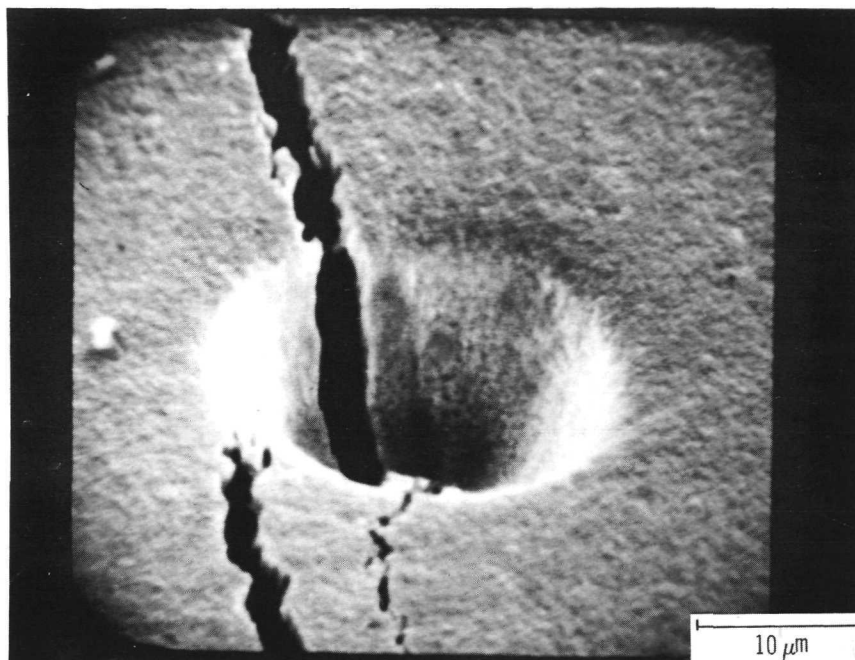
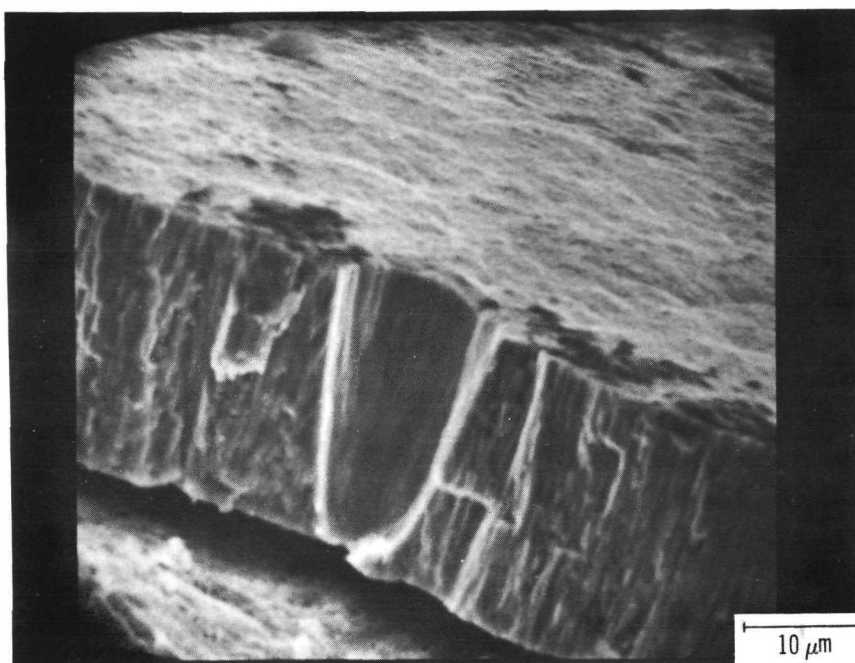


Figure 13. - Cracking around nodule after bending of sputtered S-Monel film.



(a) Surface of cavity.



(b) Cross section of cavity.

Figure 14. - Cavity in S-Monel left by ejected nodule.



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